

SMALL-ANGLE X-RAY SCATTERING INVESTIGATION OF THE EFFECT OF  
HEATING TEMPERATURE ON THE SUBMICROSCOPIC PORE STRUCTURE OF WOOD CHARCOAL\*

P. W. Schmidt, M. Kalliat\*\*,

Physics Department  
University of Missouri, Columbia, MO 65211

and B. E. Cutter

School of Forestry, Fisheries and Wildlife  
University of Missouri, Columbia, MO 65211

INTRODUCTION

One of the important advantages of x-ray techniques in structural studies is that the x-ray data can provide some information about the dimensions of the structure. Small-angle x-ray scattering, which is useful (1,2) for learning about dimensions from about 10 to 2000 Å, is an important method for investigating structures too small to be resolved by optical or scanning electron microscopy.

Small-angle x-ray scattering has been applied (3--8) in several studies of the porosity of charcoal produced by pyrolysis of wood. One of the questions considered in this research was the dependence of the pore dimensions and some other properties of the pores on the temperature to which the wood was heated during the process of pyrolysis in which the charcoal was produced.

We have already described (6-8) the results of our application of small-angle x-ray scattering in studies of several charcoals prepared by heating to temperatures not exceeding 1000°C. In order to learn about the effects of higher preparation temperatures, we recently examined a series of charcoals from black cherry (Prunus serotina Ehrh.) wood heated to temperatures from 600° to 2000°C. The results are summarized in this report.

In addition to obtaining some information about the pore structure of black cherry charcoal, we have developed a general picture of how the charcoal porosity depends on the temperature to which the wood was heated during pyrolysis. We have found (8) that for wood and for charcoal heated to temperatures not exceeding 350°C, the small-angle x-ray scattering is dominated by the scattering from crystalline cellulose, and little can be learned about the pore structure. At heating temperatures between 350° C and 400°C, this cellulose decomposes, and for charcoals prepared by heating to about 400°C, our scattering data indicate that there are large pores, called (9) macropores, with dimensions of at least a micron, transitional pores, which have dimensions of the order of a few hundred Å, and a relatively small number of much smaller pores, which, using Dubinin's terminology (9), we will refer to as micropores and which have average dimensions which do not exceed approximately 30 Å. The scattering curves which we have now obtained for charcoals prepared by heating to temperatures above 1000°C show that these higher preparation temperatures have a relatively small effect on the scattering associated with the macropores and transitional pores, but for preparation temperatures above 400°C, the scattering ascribed to the micropores increases rapidly with the preparation temperature. These results have led us to propose that the macropores in charcoals are similar to those in wood and that the main effect which pyrolysis at temperatures above 400°C exerts on the pore structure is to cause the micropores and transitional pores to grow, while leaving the macropores almost unchanged.

\*This material is based on work supported by National Science Foundation Grant No. DMR 79-03943.

\*\*Current Address: Bell Laboratories, 4500 S. Laburnum Ave., Richmond, VA 23231

## EXPERIMENTAL TECHNIQUES AND METHODS OF DATA ANALYSIS

The samples were prepared (10) by Paul R. Blankenhorn at the Pennsylvania State University School of Forest Resources by heating black cherry wood to temperatures of 600, 1500, 1750, and 2000°C in a nitrogen atmosphere.

Our scattering data were recorded by the methods discussed in Reference (8), which also reviews the corrections which we applied to the measured scattering curves.

We now will summarize some of the methods and techniques which we employed in the interpretation of our small-angle x-ray scattering data from charcoals. In a typical small-angle scattering study, x-rays from an x-ray tube are formed into a well-defined beam, usually by slits, and strike the sample. A small fraction of these x-rays are re-emitted, without change of wavelength, in directions different from that of the incoming beam. The intensity of these re-emitted x-rays, which are called the scattered rays, and their dependence on the direction in which they are emitted depend on the structure of the sample. In a scattering experiment, the intensity of the x-rays scattered in different directions is recorded, usually with some type of proportional counter. From an analysis of these data, an attempt is made to obtain information about the structure of the sample.

While there is no general prescription for analyzing the scattering pattern from an arbitrary sample, we will review some methods useful for interpretation of scattering measurements from porous materials like charcoals. For a sample which has a structure characterized by a dimension  $a$ , most information obtainable from scattering measurements will be found at scattering angles  $\theta$  in an interval for which

$$0.1 < ha < 10, \quad (1)$$

where  $h = (4\pi/\lambda) \sin(\theta/2)$ ;  $\theta$  is the scattering angle (that is, the angle between the directions of the incident and the scattered beams); and  $\lambda$  is the x-ray wavelength. For angles no greater than about 7 degrees,  $\sin \theta/2$  can be approximated by  $\theta/2$ , and so for small scattering angles,  $h$  can be considered proportional to  $\theta$ . According to Inequality 1), for a structure with dimension  $a$ , the scattering is determined by the product  $ha$ , so that there is an inverse relationship between the size of the structure and the  $h$  values at which the scattered intensity from this structure is appreciable. Since the x-ray wavelengths are normally of the order of 1 or 2 Å, Inequality 1) implies that the x-ray scattering from structures with dimensions between about 20 and 2000 Å will be observed at scattering angles no greater than a few degrees. Small-angle x-ray scattering thus can be used to study these submicroscopic structures.

X-rays are scattered by electrons, and the small-angle scattering will be appreciable when the sample contains regions in which fluctuations or variations in electron density extend over distances of 10 to 2000 Å. At small angles, the scattering process is unable to resolve structures smaller than about 10 Å, and so in the analysis of the scattering data, the atomic-scale structure can be neglected. We therefore found it convenient to consider the charcoal sample to be composed of two phases, with constant but different electron densities. One of the phases is carbonized wood, and the other is air. Because the electron density of air is so small, the scattering from the air in the pores can be neglected, and the pores can be considered to be empty.

When the two phases always are separated by a sharp, discontinuous boundary, and when  $h$  is large enough to satisfy the condition  $ha_p > 3.5$ , where  $a_p$  is the minimum characteristic dimension of the structure, the scattered intensity  $I(h)$  can be approximated by (11)

$$I(h) = \frac{2\pi\rho^2(S/M)}{h^4} \frac{M}{A} I_e A, \quad (2)$$

where  $\rho$  is the difference of the electron densities of the two phases,  $I_e$  is the intensity scattered by a single electron;  $S$  is the total surface area separating the two phases in the sample;  $M$  is the mass of the sample; and  $A$  is the cross-sectional area of the sample perpendicular to the incident beam. According to Equation 2), in

the outer part of the small-angle scattering curve (that is, when  $ha > 3.5$ ), the scattered intensity is proportional to  $h^{-4}$  and thus to the inverse fourth power of the scattering angle. Moreover, when  $I(h)$  has this angular dependence, the magnitude of the scattered intensity is proportional to the specific surface  $S/M$ , which is the surface area per unit sample mass separating the two phases.

As we explain in Reference (11), the quantities  $I_e A$  and  $M/A$  can be evaluated from the x-ray data, and so Equation 2) can be employed to calculate the specific surface  $S/M$  from the scattering data for samples with submicroscopic porosity.

The specific surface  $S/M$  calculated from Equation 2) is often referred to as the "x-ray specific surface", since it is determined from the x-ray scattering data. In this discussion of our studies of charcoal, it is important to remember that the x-ray specific surface includes only the surface of pores large enough to satisfy the condition  $ha > 3.5$ . The x-ray specific surface thus represents only the surface of the macropores and transitional pores and does not include the contribution of the micropores. This result, we believe, is the main reason why specific surfaces measured by adsorption, which often takes account of the surfaces of all three classes of pores, can be much larger than the x-ray specific surfaces.

To analyze the scattering curves which we have obtained from charcoals, we made least-squares fits of a theoretical scattering equation which contained terms representing the contributions to the scattered intensity from all three types of pores. This equation can be expressed

$$I(h) = 2\pi\rho^2 I_e A \frac{M}{A} \left[ \frac{S_1}{h^4} + \frac{S_2}{(c^{-2} + h^2)^2} + \frac{N}{2\pi M} \overline{V^2} F_m(hb) \right]. \quad (3)$$

where  $S_1$  and  $S_2$  are the surface areas per unit sample mass associated with the macropores and transitional pores;  $c$  is a constant proportional to the average characteristic dimension of the transitional pores;  $N$  is the number of micropores in the scattering sample;  $b$  is the average dimension of the micropores;  $V$  is the volume of a micropore; the bar indicates an average of  $V^2$  over the sample; and  $F_m(hb)$  is a function which describes the angular distribution of the scattering from the micropores and which is defined to have the property that  $F_m(0) = 1$ . The micropores are assumed to scatter independently of each other. The term in Equation 3) proportional to  $S_2$  describes the scattering from the transitional pores and is the expression obtained by Debye, Anderson, and Brumberger (12) for the scattering from a two-phase sample with a random distribution of scatterers. We feel that this expression is a reasonable and convenient way to approximate the scattering from the transitional pores. The macropore scattering is represented in Equation 3) by the term proportional to  $S_1$ . The macropores are so large that our scattering data permit only the calculation of the specific surface of these pores and provide no information about their dimensions.

## RESULTS AND DISCUSSION

Figure 1 shows the scattering curves which we obtained for southern pine wood heated to 400°C at different rates (8). When the sample temperature was raised at a rate of 50°C per minute, the scattering pattern was quite similar to the curve obtained for wood before heating. For a temperature rise of only 1°C per minute, on the other hand, the inner part of the scattering curve is nearly proportional to the inverse fourth power of  $h$ , as would be expected for the scattering from macropores, while in the outer part of the scattering curve, the intensity is nearly constant, as we would predict for micropores. The third curve in Fig. 1 is for a sample with a temperature increase of 10°C per minute and is intermediate between the other two curves. We have shown (8) that the change from a curve like the curve for a heating rate of 50°C/min to a curve with the form of the curve for 1°C/min is accompanied by the disappearance of the large-angle diffraction peaks from cellulose. We have therefore concluded that the curve for a heating rate of 1°C/min represents the scattering from only the pores in the charcoal.

Figure 2 shows the scattering curves for black cherry samples heated to

temperatures of 600, 1500, 1750, and 2000°C. Regardless of the temperature at which the sample was prepared, the inner part of the scattering curve is nearly proportional to  $h^{-4}$ . This region of the curve is almost the same for all heating temperatures, but the intensity in the outer part of the curve rises as the heating temperature is increased. This part of the curve contains the information about the micropores.

The curves in Fig. 2 were determined by least-squares fits of Equation (3) to the scattering data for the black cherry charcoals. In the fits of the scattering data recorded for samples produced at 1500°C and above, for  $F_m(hb)$  we used the function  $P_2(h, l)$  calculated (13) for assemblies of uniform spherical scatterers with different diameters. With this fitting function, we obtained at least an adequate fit. In our analysis of the curve for the sample heated at 600°C we employed an  $F_m(hb)$  function of the same form as the function chosen to represent the scattering from the transitional pores. We multiplied the average micropore dimension obtained in this fit by a constant which permitted this  $b$  value to be compared with the other average micropore dimensions.

As can be seen from Table 1, which lists some of the quantities obtained from the least-squares fits of Equation (3), when the preparation temperature is raised from 600°C to 2000°C, the constant

$$B = \frac{N}{2\pi M} \overline{V^2}, \quad (4)$$

which expresses the magnitude of the scattering from the micropores, increases by a factor of almost 50, while the average micropore dimension  $b$  is not even doubled. [The rather unusual units  $\text{cm}^3 \text{Å}^3/\text{gm}$  used for  $B$  are convenient for some analyses discussed in Reference (8).] If the shape of the micropores is independent of the preparation temperature, the square of the volume of a pore is proportional to  $b^3$ , and according to Equation 4),  $B/b^6$  should be proportional to  $N/M$ , the number of pores per unit mass. From the values of  $B$  and  $b$  in Table 1, as the temperature of sample preparation increases from 600°C to 2000°C,  $B/b^6$  varies by about 30% around its average value for the four samples. Within the relatively large uncertainty resulting from the fact that  $b$  is raised to the sixth power,  $B/b^6$  thus is independent of the pyrolysis temperature. We therefore can consider that the number of micropores, which according to Equation 4) is proportional to  $B/b^6$ , remains very nearly constant, so that higher pyrolysis temperatures lead to charcoals with larger micropores, but the number of micropores does not change appreciably.

In our discussion of data analysis, we have avoided making any precise statements about the meaning of the average pore dimensions, since the definition of these average dimensions depends on the pore shape and on the distribution of pore dimensions. However, Equation 3) contains terms which give the scattering from the three classes of pores. The models used to obtain the terms for the contributions from the transitional pores and micropores specify what the average pore dimensions represent in these models. In the expression for  $F_m(hb)$  which we used to describe the scattering from the micropores for preparation temperatures of 1500°C and above,  $b$  is the most probable micropore radius in a system of independently-scattering spheres with different radii. The interpretation of the other average dimensions is discussed in Reference (12).

The quantities  $S_1$ ,  $S_2$ , and  $B$  were evaluated by the techniques we employed in our investigation of southern pine charcoal (8). In our calculations, we assumed (8) that the density of the carbon in the charcoals was  $\text{gm/cm}^3$ , while we took the mass absorption coefficient of carbon to be  $4.60 \text{ cm}^2/\text{gm}$ .

In Table 1 we show only the total x-ray specific surface ( $S_1 + S_2$ ), since we found that the region of the scattering curve which was nearly proportional to the inverse fourth power of  $h$  was not long enough to permit a good separation of the contributions of the macropores and transitional pores to the total x-ray specific surface. We estimate that the uncertainty in the x-ray specific surfaces in about 25%. Since the x-ray specific surface  $S_1 + S_2$  is so nearly the same in all four samples, we suggest that the macropore structure in the charcoal samples is almost the same as in the wood from what the charcoals were prepared.

While the uncertainty in the value of  $c$  computed from the least squares fits increases to about  $\pm 50\%$  for the sample heated to 2000°C, our fits show a steady

growth in the average dimension  $c$  of the transitional pores as the preparation temperature becomes higher.

Unfortunately, we were not able to obtain black cherry samples heated to temperatures between 600°C and 1500°C. Samples prepared in this temperature interval would probably give a more detailed description of the effect of pyrolysis temperature on the number and average dimension of the micropores.

We feel, however, that the scattering curves which we have presented here are sufficient to support our views about the relation between the pore structure and the temperature at which the sample was prepared. From our analysis of the scattering data, we have concluded that when the charcoals are prepared by heating to 400°C, most of the scattering comes from the macropores and transitional pores, with a relatively small contribution from the micropores, the dimensions of which are not large enough to be determined reliably from the scattering data. For pyrolysis at temperatures in the interval from 400°C through 2000°C, the transitional pores and micropores become larger, while the x-ray specific surface and the number of micropores remain nearly the same.

#### ACKNOWLEDGMENTS

We are very grateful to Paul R. Blankenhorn for preparing the charcoal samples.

#### REFERENCES

1. Guinier, A.; Fournet, G.; Walker, C. B.; Yudowitch, K. L.; "Small-Angle Scattering of X-Rays"; Wiley: New York, 1955.
2. Glatter, O., and Kratky, O.; "Small Angle Scattering of X-Rays"; Academic Press: New York, 1982.
3. János, A.; Stoeckli, H. F. Carbon 1979, 17, 465-469.
4. Hernández, J. G.; Hernández-Calderón, I.; Luengo, C. A.; Tsu, R. Carbon 1982, 20, 201-205.
5. González, J. H.; Torriani, I. L.; Luengo, C. A. J. Appl. Cryst. 1982, 15, 251-254.
6. Von Bastian, C. R.; Schmidt, P. W.; Szopa, P. S.; McGinnes, E. A., Jr. Wood and Fiber 1972, 4, 185-192.
7. Casteel, J. L.; Pringle, O. A., Jr.; Lin, J. S.; Schmidt, P. W.; Slocum, D. H.; McGinnes, E. A., Jr. Wood and Fiber 1978, 10, 6-18.
8. Kalliat, M.; Cutter, B. E.; Kwak, C. Y.; Schmidt, P. W.; McGinnes, E. A., Jr. Wood Science and Technology, in press.
9. Dubinin, M. M.; in "Chemistry and Physics of Carbons"; Walker, P. L., Jr., ed.; Vol II; Dekker: New York, 1954; pp. 51-59.
10. Blankenhorn, P. R.; Barnes, D. P.; Kline, D. E.; Murphey, W. K. Wood Sci. 1978 11, 23-29.
11. Kalliat, M.; Kwak, C. Y.; Schmidt, P. W.; in "New Approaches to Coal Chemistry"; Blaustein, B. D.; Bockrath, B. C.; Friedman, S., eds.; ACS Symposium Series No. 169; Amer. Chem. Soc.: Washington, 1981; pp. 3-22.
12. Debye, P.; Brumberger, H.; Anderson, H. L., Jr. J. Appl. Phys. 1957, 28, 679-683.
13. Schmidt, P. W. Acta Cryst. 1958, 11, 675.

TABLE 1  
Quantities Evaluated from the Least-Squares Fits

Pyrolysis Temperature	$S_{12} + S_2$ ( $m^2/gm$ )	$B(cm^3\text{\AA}^3/gm)$	$b(\text{\AA})$	$c(\text{\AA})$
600°C	1.6	2.9	1.3	$0.33 \times 10^2$
1500	1.7	60	2.0	$0.76 \times 10^2$
1750	1.9	87	2.1	2.2
2000	1.8	122	2.4	5.3

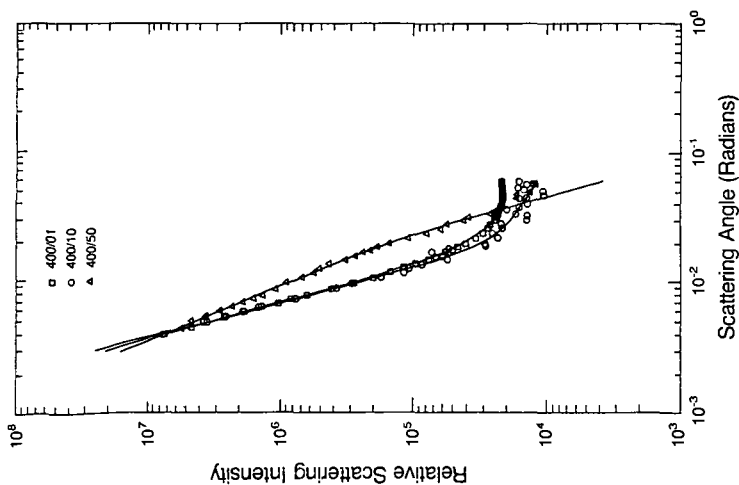


Figure 1. Scattering curve for charcoals produced by increasing the temperature to 400°C at rates of 1 (squares), 10 (circles), and 50 (triangles) degrees C per minute. (Reproduced by permission from Ref. 8.)

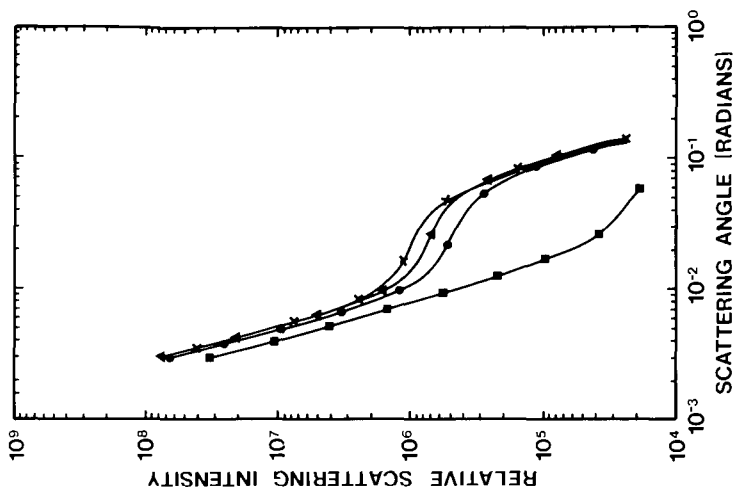


Figure 2. Scattering curves for black cherry charcoal pyrolyzed at temperatures of 600 (squares), 1500 (circles), 1750 (triangles) and 2000 (crosses) degrees C. The curves were obtained by least-squares fits of Eq. 3).